

The X-ray Single-Crystal and Molecular Structures of $[\text{Co}_2(\text{CO})_6\text{C}_2\text{R}_2]$ for $R = \text{Ph}$ (I), CO_2Me (II) (292 K) and $R = \text{Bu}^t$ (III) (200 K)*

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Abstract. (I) $M_r = 464.1$, monoclinic, Cc , $a = 15.990$ (3), $b = 16.008$ (3), $c = 8.005$ (1) Å, $\beta = 107.62$ (1)°, $V = 1952.9$ (7) Å³, $Z = 4$, $\mu(\text{Mo } K\alpha) = 17.3$ cm⁻¹, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $D_x = 1.58$ g cm⁻³, $T = 292$ K, $F(000) = 927.8$. (II) $M_r = 428.0$, monoclinic, $P2_1/n$, $a = 7.660$ (1), $b = 14.405$ (3), $c = 15.892$ (5) Å, $\beta = 104.03$ (2)°, $V = 1701.2$ (7) Å³, $Z = 4$, $\mu(\text{Mo } K\alpha) = 20.7$ cm⁻¹, $D_x = 1.77$ g cm⁻³, $T = 292$ K, $F(000) = 847.8$. (III) $M_r = 424.0$, triclinic, $P\bar{1}$, $a = 8.292$ (1), $b = 8.408$ (2), $c = 13.586$ (3) Å, $\alpha = 88.66$ (2), $\beta = 94.48$ (2), $\gamma = 106.74$ (1)°, $V = 904.2$ Å³, $Z = 2$, $\mu(\text{Mo } K\alpha) = 18.6$ cm⁻¹, $D_x = 1.56$ g cm⁻³, $T = 200$ K, $F(000) = 431.9$. Final R values 0.055, 0.073 and 0.025 for 1576, 881 and 2221 reflections [(I), (II) and (III) respectively]. The 'sawhorse' geometry of the $(\text{OC})_3\text{Co}-(\text{CO})_3$ fragment is reconfirmed with Co–Co separations of 2.476 (2) (I), 2.477 (3) (II), and 2.460 (1) Å (III), and the coordinated C–C bond distances of 1.36 (1) (I), 1.33 (3) (II) and 1.341 (3) Å (III) respectively. The differences in these and other molecular parameters can be related to the changes in the substituent group R of the coordinated acetylene molecule.

Introduction. The investigation of the title complexes and the redetermination of the structures of two of them, namely (I) $\text{C}_2\text{Ph}_2 = R$ (Sly, 1959) and (II) $\text{Bu}^t = R$ (Cotton, Jamerson & Stults, 1976), was prompted by our interest in determining experimental electron densities in selected dimers of the first-row transition metals. It was necessary first to assess several $[\text{Co}_2(\text{CO})_6\text{C}_2\text{R}_2]$ complexes with different substituents R in order to optimize the experimental parameters required for the extended low-temperature X-ray diffraction study and the neutron-diffraction experiment which were both carried out at the same temperature.

* (I) Bis(μ -diphenylacetylene)-bis(tricarbonylcobalt)(Co–Co), $[\text{Co}_2(\text{C}_{14}\text{H}_{10})(\text{CO})_6]$, (II) bis(μ -(dimethyl 2-butyndioate))-bis(tricarbonylcobalt)(Co–Co), $[\text{Co}_2(\text{C}_8\text{H}_6\text{O}_4)(\text{CO})_6]$, (III) bis(μ -(2,2,5,5-tetramethyl-3-hexyne))-bis(tricarbonylcobalt)(Co–Co), $[\text{Co}_2(\text{C}_{10}\text{H}_{18})(\text{CO})_6]$.

The full details of this electron-density study will be published at a later date; we herein report briefly the X-ray structures for the three acetylene complexes studied.

We were looking for crystallization in a centrosymmetric space group of relatively small unit-cell volume, the potential for growth to a large single crystal, moderate solid-state stability with no disorder, or phase change on cooling. These criteria were best satisfied by $R = \text{Bu}^t$ and although both room-temperature and 200 K data were collected, only the latter are reported in this paper.

It was possible that for $R = \text{Ph}$ the complex could crystallize in the centrosymmetric space group $C2/c$, rather than Cc , but this hope was unfounded and the problem was investigated no further. However, our results reported herein are more accurate than the earlier structural study (Sly, 1959).

Experimental. The complexes were prepared by the reaction between the appropriate acetylene (C_2R_2) and $[\text{Co}_2(\text{CO})_8]$ according to the literature methods (Cotton *et al.*, 1976, and references therein).

The experimental details given for the X-ray data collection (see Table 1) are common to each study unless specifically stated otherwise: Nicolet $P3m$ automated four-circle diffractometer, cold stream of dry nitrogen gas collinear with the crystal ϕ axis for cooling the sample (III). Since the criteria given above were optimized for $R = \text{Bu}^t$, only this sample was cooled following the initial room-temperature study to test its thermal stability. Scattering factors from *International Tables for X-ray Crystallography* (1974), all computations carried out using *SHELXTL* (Sheldrick, 1981) on a Data General Eclipse S230 computer.

Discussion. The following discussion applies to the molecular parameters determined at room temperature (292 K) for (I) and (II), whereas those given for (III) are taken from the low-temperature study (200 K). Figs. 1–3 illustrate the molecular geometry of each

complex with given numbering schemes, the parameters for which are listed in Tables 2 and 3. All atomic coordinates are given in Table 4.*

* A list of structure factors, tables of least-squares planes, all thermal parameters and all bond lengths and angles, and, for (III), the molecular geometry associated with the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38554 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental data for* $[\text{Co}_2(\text{CO})_6(\text{C}_2\text{R}_2)]$

<i>R</i>	(I) C_6H_5	(II) CO_2Me	(III) Bu^t
D_m (g cm ⁻³)	Not measured	Not measured	1.55
Crystal shape	Needle	Prismatic	Needle
size	Not measured	Not measured	Not measured
Absorption correction	Not applied	Not applied	Not applied
N (range)*	13(5.6 ≤ θ ≤ 11.9°)	15(5.5 ≤ θ ≤ 11.8°)	11(12.3 ≤ θ ≤ 16.2°)
h, k, l	min. 0, 0, 1 max. 22, 23, 11	0, 0, 15 7, 13, 14	0, 9, 14 8, 9, 14
Standard reflections	5 $\bar{3}$ 2, 3 $\bar{1}$ 2	1 $\bar{1}$ 4, 23 $\bar{1}$	4 $\bar{5}$ 3, 5 $\bar{2}$ 3, 5 4 3
% variation	2.0	14.0	3.0
Total reflections measured	1875	1861	2573
$2\theta_{\text{max}}$ (°)	50	40	45
Independent data	1789	1180	2260
Data used	1576	881	2221
$I > n\sigma(I)$: n	1	1.5	1
R_{int}	0.032	0.043	0.023
H atoms	Located; not refined	Not located	Located; refined
Weighting scheme			
$[\sigma^2(F)] + g F^2 ^{-1}$: g	0.00085	0.001	0.0002
Scan type	$\omega:2\theta$	$\omega:2\theta$	$\omega:2\theta$
Refinement	Block cascaded least squares, $\sum w(\Delta F)^2$ minimized		
R (R^1)	0.055(0.053)	0.073(0.073)	0.025(0.027)
S	1.21	1.85	1.88
Maximum (shift:error)	-0.001	-0.011	+0.017
$\Delta\rho$ (max:min) (e Å ⁻³)	0.07:-0.3	0.75:-0.6	0.66:-0.33

* Number of reflections for lattice-parameter calculations and θ ranges.

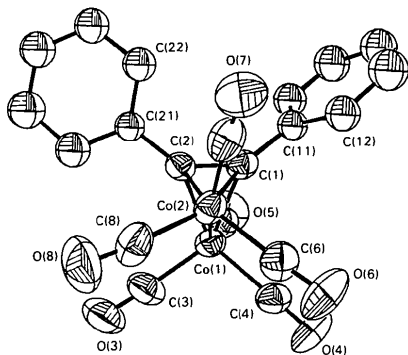


Fig. 1. Molecular structure of $[\text{Co}_2(\text{CO})_6(\text{C}_2\text{Ph}_2)]$ (I) viewed almost perpendicular to the mean plane of the diphenylacetylene ligand.

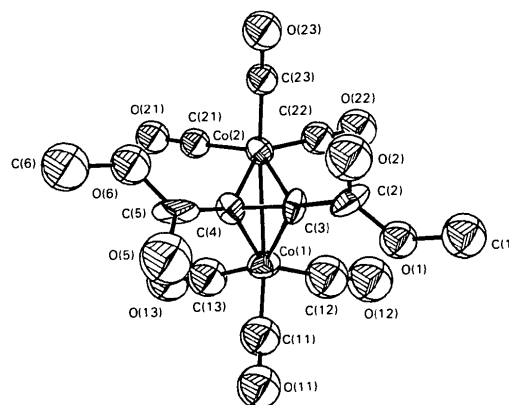


Fig. 2. Molecular structure of $[\text{Co}_2(\text{CO})_6\{(\text{CO}_2\text{Me})_2\text{C}_2\}]$ (II) showing the orthogonal arrangement of the Co-Co and C-C vectors.

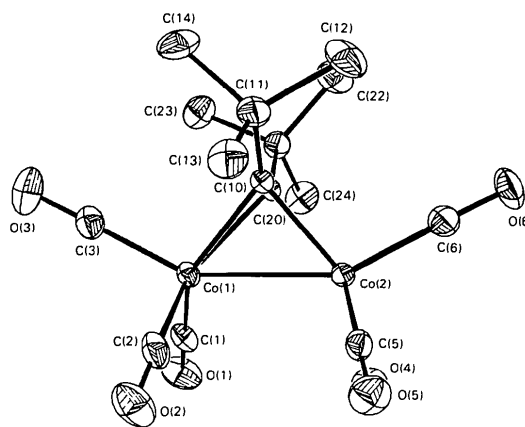


Fig. 3. Molecular structure of $[\text{Co}_2(\text{CO})_6(\text{C}_2\text{Bu}_2^t)]$ (III) showing the 'sawhorse' geometry of the ' $\text{Co}_2(\text{CO})_6$ ' framework.

The previously established geometry of these μ -acetylene complexes is reconfirmed with the C-C bond of the bridging acetylene lying perpendicular to the Co-Co vector in all three cases [92 (I), 89 (II), 90° (III)]. There are, however, some interesting variations in the molecular parameters, which can be related to the changing nature of the substituent R on the acetylene. As the electron-withdrawing character of R is increased we would expect a longer C-C bond and a shorter Co-C(R) separation. This follows from a shift in energy of both the π and π^* orbitals on the acetylene with a modification of the electron density at the ligated C atom (Thorn & Hoffmann, 1978; Anderson, 1976). Increased back donation from the metal atoms to the acetylene π^* orbitals decreases the M-C and increases the C-C distances. Unfortunately the experimental errors on the C-C bond lengths for (I) and (II) [0.01 (I), 0.02 Å (II)] are such that there is not a significant difference between them, whereas the more

Table 2. Summary of important molecular parameters for [Co₂(CO)₆C₂R₂]

	(I)	(II)	(III)
Co—Co (Å)	2.476 (2) Å	2.477 (3) Å	2.460 (1) Å
Co—μ(C) mean	1.97 (1)	1.92 (2)	1.987 (2)
C=C	1.36 (1)	1.33 (3)	1.341 (3)
μC—R	1.46 (1)	1.42 (3)	1.515 (3)
Co—C(O)	1.80 (1)	1.72 (3)	1.789 (2)
Co—C(O) <i>cis</i>	1.82 (1)	1.76 (3)	1.822 (2)
C—C—R (mean)	140.2 (9)°	139 (2)°	144.4 (1)°
Co—Co—C(O)	147.9 (4)	148.5 (8)	152.2 (1)
C—Co—C(O) (<i>cis</i>)	105.6 (5)	104 (1)	103.9 (1)

sensitive M—C distances are in accord with this hypothesis [(I) 1.97 (2), (II) 1.92 (1), (III) 1.987 (2) Å]. The data for the corresponding complex with R = CF₃ (Baert & Coppens, 1982) effectively also fit this pattern, with a C—C of 1.36 Å and Co—C (mean) of 1.93 Å, respectively [Co—C separations (8) range from 1.925 to 1.935 (5) Å].

A concomitant effect is observed in the R—C≡C angles and the R—C(≡C) distances which are similarly dependent on the density distribution at the attached C

Table 3. Selected bond lengths (Å) and interbond angles (°) with estimated standard deviations in parentheses for [Co₂(CO)₆(C₂R₂)]

(I) R = phenyl			
Co(1)—Co(2)	2.476 (2)	Co(1)—C(1)—Co(2)	77.2 (4)
Co(1)—C(1)	2.022 (10)	Co(1)—C(2)—Co(2)	78.5 (3)
Co(1)—C(2)	1.960 (10)	Co(1)—Co(1)—C(2)	39.9 (4)
Co(2)—C(1)	1.948 (10)	C(1)—Co(2)—C(2)	40.8 (4)
Co(2)—C(2)	1.952 (8)	Co(1)—Co(2)—C(7)	149.2 (4)
Co(1)—C(3)	1.775 (15)	Co(2)—Co(1)—C(5)	146.6 (4)
Co(1)—C(4)	1.863 (13)	C(3)—Co(1)—C(4)	104.5 (6)
Co(1)—C(5)	1.787 (12)	C(6)—Co(2)—C(8)	106.8 (5)
Co(2)—C(6)	1.854 (12)		
Co(2)—C(7)	1.820 (13)		
Co(2)—C(8)	1.798 (14)		
C(3)—O(3)	1.13 (2)	Co(1)—C(3)—O(3)	178 (1)
C(4)—O(4)	1.12 (2)	Co(1)—C(4)—O(4)	179 (1)
C(5)—O(5)	1.13 (1)	Co(1)—C(5)—O(5)	179 (1)
C(6)—O(6)	1.12 (1)	Co(2)—C(6)—O(6)	178 (1)
C(7)—O(7)	1.14 (2)	Co(2)—C(7)—O(7)	176 (1)
C(8)—O(8)	1.13 (2)	Co(2)—C(8)—O(8)	175 (1)
C(1)—C(11)	1.470 (15)	C(2)—C(1)—C(11)	140 (1)
C(2)—C(21)	1.458 (14)	C(1)—C(2)—C(21)	140 (1)
C—C(φ) mean	1.39 (2)	C—C—C(φ) mean	120 (1)
(II) R = CO ₂ Me			
Co(1)—Co(2)	2.477 (3)	Co(1)—C(3)—Co(2)	79.7 (7)
Co(1)—C(3)	1.93 (2)	Co(1)—C(4)—Co(2)	80.7 (7)
Co(1)—C(4)	1.92 (2)	C(3)—Co(1)—C(4)	40.5 (7)
Co(2)—C(3)	1.93 (2)	C(3)—Co(2)—C(4)	40.7 (7)
Co(2)—C(4)	1.91 (2)	Co(2)—Co(1)—C(11)	149.1 (8)
C(3)—C(4)	1.33 (3)	Co(1)—Co(2)—C(23)	148.0 (7)
Co(1)—C(11)	1.70 (3)	C(21)—Co(2)—C(22)	105 (1)
Co(1)—C(12)	1.73 (3)	C(13)—Co(1)—C(12)	104 (1)
Co(1)—C(13)	1.74 (3)		
Co(2)—C(21)	1.80 (3)	C(3)—C(4)—C(5)	139 (2)
Co(2)—C(22)	1.75 (3)	C(2)—C(3)—C(4)	139 (2)
Co(2)—C(23)	1.74 (3)	C(4)—C(5)—O(5)	123 (3)
C(3)—C(2)	1.44 (3)	C(4)—C(5)—O(6)	120 (2)
C(2)—O(1)	1.26 (3)	C(3)—C(2)—O(2)	119 (1)
O(1)—C(1)	1.50 (3)	C(3)—C(2)—O(1)	119 (1)
C(2)—O(2)	1.24 (3)	C(2)—O(1)—C(1)	118 (2)
C(4)—C(5)	1.40 (3)	C(5)—O(6)—C(6)	119 (2)
C(5)—O(6)	1.29 (3)		
O(6)—C(6)	1.50 (3)		
C(5)—O(5)	1.22 (3)		
C—O mean	1.18 (3) (carbonyl)	Co—C—O mean	174 (2)
(III) R = Bu ^t			
Co(1)—Co(2)	2.460 (1)	Co(1)—C(10)—Co(2)	76.6 (1)
Co(1)—C(10)	1.988 (2)	Co(1)—C(20)—Co(2)	76.4 (1)
Co(1)—C(20)	1.992 (2)	C(10)—Co(1)—C(20)	39.4 (1)
Co(2)—C(10)	1.982 (2)	C(10)—Co(2)—C(20)	39.5 (1)
Co(2)—C(20)	1.985 (2)	Co(1)—Co(2)—C(6)	152.0 (1)
C(10)—C(20)	1.341 (3)	Co(2)—Co(1)—C(3)	152.5 (1)
Co(1)—C(1)	1.812 (2)	C(1)—Co(1)—C(2)	103.6 (1)
Co(1)—C(2)	1.826 (2)	C(4)—Co(2)—C(5)	104.3 (1)
Co(1)—C(3)	1.790 (2)		
Co(2)—C(4)	1.828 (2)	C(11)—C(10)—C(20)	144.1 (2)
Co(2)—C(5)	1.822 (2)	C(21)—C(20)—C(10)	144.8 (2)
Co(2)—C(6)	1.788 (3)		
C(10)—C(11)	1.516 (3)		
C(20)—C(21)	1.515 (3)		
C—C(Bu ^t) mean	1.531 (3)	C—C—C (Bu ^t) mean	109.5 (2)
C—O mean	1.137 (3)	Co—C—O mean	179.1 (2)

Table 4. Atomic positional (fractional coordinates) and thermal parameters with estimated standard deviations in parentheses

An asterisk denotes $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

(I) R = phenyl				U or U _{eq}
	x	y	z	(Å ² × 10 ³)
Co(1)	0.00000	0.14952 (8)	0.00000	4.71 (5)*
Co(2)	0.10982 (10)	0.22141 (8)	0.2434 (3)	4.84 (5)*
C(1)	0.0517 (6)	0.2653 (6)	0.0101 (14)	4.7 (4)*
C(2)	-0.0063 (6)	0.2594 (6)	0.1034 (13)	4.3 (4)*
C(12)	0.1583 (7)	0.3427 (8)	-0.0982 (15)	6.1 (3)
C(13)	0.1777 (9)	0.4023 (10)	-0.216 (2)	8.1 (4)
C(14)	0.1085 (9)	0.4301 (9)	-0.356 (2)	7.4 (4)
C(15)	0.0244 (9)	0.4031 (9)	-0.383 (2)	7.4 (4)
C(16)	0.0062 (7)	0.3492 (8)	-0.2638 (15)	6.0 (3)
C(11)	0.0727 (6)	0.3196 (7)	-0.1200 (14)	4.7 (3)
C(22)	-0.0785 (7)	0.3942 (7)	0.1099 (14)	5.6 (3)
C(23)	-0.1420 (7)	0.4437 (8)	0.1512 (15)	6.2 (3)
C(24)	-0.2015 (8)	0.4074 (8)	0.220 (2)	6.8 (4)
C(25)	-0.1973 (9)	0.3233 (9)	0.261 (2)	7.4 (4)
C(26)	-0.1319 (7)	0.2724 (8)	0.2230 (15)	6.1 (3)
C(21)	-0.0735 (6)	0.3089 (6)	0.1464 (13)	4.5 (3)
C(3)	-0.0528 (9)	0.0830 (8)	0.114 (2)	7.1 (6)*
O(3)	-0.0887 (7)	0.0426 (7)	0.186 (2)	10.4 (6)*
C(4)	0.0771 (8)	0.0797 (7)	-0.068 (2)	5.8 (5)*
O(4)	0.1239 (6)	0.0373 (7)	-0.1061 (13)	9.1 (5)*
C(5)	-0.0802 (8)	0.1595 (8)	-0.210 (2)	7.1 (6)*
O(5)	-0.1310 (7)	0.1651 (8)	-0.3425 (14)	10.1 (5)*
C(6)	0.2088 (7)	0.1657 (8)	0.2275 (15)	6.1 (5)*
O(6)	0.2682 (6)	0.1329 (7)	0.2119 (14)	9.5 (5)*
C(7)	0.1705 (8)	0.3159 (9)	0.3316 (15)	6.5 (5)*
O(7)	0.2115 (8)	0.3739 (6)	0.3815 (15)	9.8 (5)*
C(8)	0.0843 (8)	0.1790 (9)	0.430 (2)	7.1 (5)*
O(8)	0.0626 (8)	0.1556 (9)	0.5440 (15)	11.4 (6)*
(II) R = CO ₂ Me				U or U _{eq}
	x	y	z	(Å ² × 10 ³)
Co(1)	0.1961 (4)	0.2062 (2)	0.32165 (14)	6.44 (12)*
Co(2)	0.4327 (3)	0.3022 (2)	0.4163 (14)	5.26 (10)*
C(1)	0.140 (4)	0.070 (2)	0.6039 (15)	11.9 (13)*
C(2)	0.202 (3)	0.1975 (14)	0.5212 (12)	7.5 (10)*
C(3)	0.231 (3)	0.2382 (12)	0.4428 (11)	5.0 (8)*
C(4)	0.177 (3)	0.3120 (13)	0.3926 (11)	5.3 (8)*
C(5)	0.054 (3)	0.385 (2)	0.3850 (14)	9.4 (11)*
C(6)	-0.022 (4)	0.548 (2)	0.378 (2)	12.4 (9)
O(1)	0.171 (2)	0.1118 (11)	0.5222 (9)	8.3 (5)
O(2)	0.196 (3)	0.2484 (13)	0.5836 (11)	11.7 (6)
O(5)	-0.108 (3)	0.3736 (14)	0.3747 (12)	15.0 (7)
O(6)	0.111 (2)	0.4702 (12)	0.3896 (9)	9.5 (5)
C(11)	-0.023 (3)	0.1714 (15)	0.2921 (15)	10.2 (8)
O(3)	-0.176 (2)	0.1498 (11)	0.2794 (11)	11.7 (6)
C(12)	0.298 (4)	0.099 (2)	0.328 (2)	14.0 (10)
O(12)	0.377 (3)	0.0260 (15)	0.3382 (13)	16.7 (8)
C(13)	0.209 (4)	0.248 (2)	0.221 (2)	11.2 (9)
O(13)	0.222 (3)	0.2866 (14)	0.1562 (12)	14.8 (7)
C(21)	0.485 (3)	0.3770 (14)	0.3346 (13)	6.8 (6)
O(21)	0.505 (2)	0.4325 (10)	0.2868 (9)	9.0 (5)
C(22)	0.608 (3)	0.2209 (15)	0.4389 (13)	8.2 (7)
O(22)	0.728 (3)	0.1655 (12)	0.4578 (11)	12.5 (6)
C(23)	0.500 (3)	0.3682 (14)	0.5100 (13)	6.4 (6)
O(23)	0.526 (2)	0.4133 (11)	0.5732 (10)	9.6 (5)

Table 4 (cont.)

(III) $R = \text{Bu}'$	x	y	z	U_{eq}^\dagger ($\text{\AA}^2 \times 10^3$)
Co(1)	0.24494 (3)	0.04942 (3)	0.23987 (2)	1.634 (9)
Co(2)	0.09764 (3)	0.24190 (3)	0.16352 (2)	1.582 (9)
C(1)	0.0646 (3)	-0.1114 (3)	0.27963 (15)	2.32 (8)
O(1)	-0.0480 (3)	-0.2115 (2)	0.30599 (13)	3.87 (7)
C(2)	0.2932 (3)	-0.0347 (3)	0.1267 (2)	2.52 (8)
O(2)	0.3197 (3)	-0.0889 (3)	0.05592 (13)	4.00 (7)
C(3)	0.4052 (3)	0.0026 (3)	0.3216 (2)	2.64 (9)
O(3)	0.5053 (3)	-0.0303 (3)	0.37374 (14)	4.64 (8)
C(4)	-0.1177 (3)	0.1149 (3)	0.1809 (2)	2.29 (8)
O(4)	-0.2508 (2)	0.0352 (2)	0.19206 (12)	3.41 (7)
C(5)	0.1257 (3)	0.2116 (3)	0.0343 (2)	2.10 (8)
O(5)	0.1430 (2)	0.1921 (2)	-0.04617 (11)	3.23 (6)
C(6)	0.0629 (3)	0.4419 (3)	0.1516 (2)	2.52 (9)
O(6)	0.0388 (3)	0.5682 (3)	0.14203 (14)	4.17 (7)
C(10)	0.3296 (3)	0.2950 (3)	0.22794 (14)	1.64 (7)
C(11)	0.4978 (3)	0.4126 (3)	0.2032 (2)	2.30 (8)
C(12)	0.4803 (4)	0.5886 (3)	0.1876 (2)	3.46 (10)
C(13)	0.5566 (3)	0.3591 (3)	0.1090 (2)	2.77 (8)
C(14)	0.6286 (3)	0.4132 (4)	0.2889 (2)	3.25 (9)
C(20)	0.2172 (3)	0.2552 (3)	0.29683 (15)	1.70 (7)
C(21)	0.1775 (3)	0.2983 (3)	0.39810 (15)	2.25 (8)
C(22)	0.2142 (4)	0.4869 (3)	0.4065 (2)	3.61 (10)
C(23)	0.2912 (3)	0.2396 (4)	0.4770 (2)	3.09 (9)
C(24)	-0.0068 (3)	0.2150 (4)	0.4170 (2)	3.18 (9)

† All atoms anisotropically refined.

atoms, assumed to be sp^2 , sp^2 and sp^3 hybridized respectively for (I), (II) and (III). Both increase as expected in the order $R = -\text{CO}_2\text{Me}$, $-\text{Ph}$, $-\text{Bu}'$, with values of 139, 140, 144° and 1.42 (3), 1.46 (1) and 1.515 (3) \AA , respectively. The equivalent values for $R = \text{CF}_3$ are 139° and 1.48 \AA . For (I) and (II) the degree of delocalization suggested by the short $R-\text{C}(\equiv\text{C})$ is echoed by the approximate coplanarity of each $\text{C}-R$ group [maximum deviation 0.02 (I), 0.01 (II) \AA for R -group atoms and 0.1 (I), 0.6 (II) \AA for C atoms] although each group is twisted relative to the mean plane of its acetylene [dihedral angles 47, 61 (I) and 52, 19° (II)]. These somewhat random orientations are assumed to derive from steric factors,

since with such arrangements there are no short intramolecular contacts. In (III) any close methyl $\text{H}\cdots\text{H}$ contacts are minimized by a semi-staggered conformation of the Bu' groups, with respect to the $\text{C}-\text{C}$ vector.

The $\text{Co}-\text{Co}$ separations are also sensitive to R and in good agreement with previously recorded $\text{Co}-\text{Co}$ single-bond distances (Leung, Coppens, McMullan & Koetzle, 1981; Teller, Wilson, McMullan, Koetzle & Bau, 1978; Cirjak, Ginsberg & Dahl, 1982). The bend of the ' $\text{Co}_2(\text{CO})_2$ ' spine (Fig. 3) is more acute for (I) and (II), 148° , than for (III), 152° .

All three structures show a shorter 'axial' (*trans* to $\text{Co}-\text{Co}$ bond) $M-\text{C}(\text{O})$ bond length than those of the 'cis' equatorial ligands (Table 2), the latter adopting an eclipsed configuration.

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Hexakis(imidazole)manganese(II) Dichloride Tetrahydrate, $[\text{Mn}(\text{C}_3\text{H}_4\text{N}_2)_6]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, and Hexakis(imidazole)zinc(II) Dichloride Tetrahydrate, $[\text{Zn}(\text{C}_3\text{H}_4\text{N}_2)_6]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$

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Abstract. $[\text{Mn}(\text{ImH})_6]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (ImH = imidazole, $\text{C}_3\text{H}_4\text{N}_2$): $M_r = 606.4$, triclinic, $P\bar{1}$, $a = 10.726$ (3), $b = 9.275$ (2), $c = 8.846$ (2) \AA , $\alpha = 119.65$ (1), $\beta =$

96.87 (2), $\gamma = 97.62$ (2)°, $V = 740.3$ (4) \AA^3 , $Z = 1$, $D_m = 1.37$ (1), $D_x = 1.360$ g cm^{-3} , $\lambda(\text{Mo } K\alpha) = 0.71069$ \AA , $\mu(\text{Mo } K\alpha) = 6.53$ cm^{-1} , $F(000) = 315$, $T = 291$ K, $R = 0.030$ for 3542 unique reflections. $[\text{Zn}(\text{ImH})_6]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$: $M_r = 616.8$, triclinic, $P\bar{1}$, $a =$

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